Towards the hydrogenation of oils in monolith reactor: methodology for washcoat development and performance evaluation

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Context: GLS hydrogenation

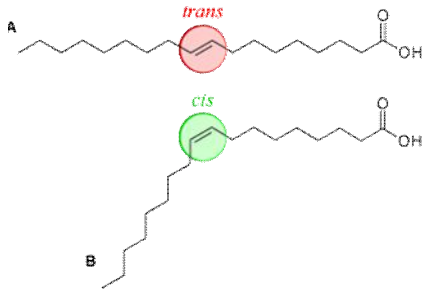
Significant class of reactions:

for the production of fine chemicals, pharmaceuticals, flavors and fragrances, the conversion of biomass and the processing of raw food

But several issues:

- **fast reactions**, thus prone to mass transfer limitations
- **highly exothermic reactions** ($\Delta H_R \approx$ -100–130 kJ/mol$_=$), resulting in possible thermal hazards
- **selectivity constraints**, due to consecutive reaction scheme and parallel side reactions (e.g. cis-trans isomerization)

ex. in food industry: C18:3 → C18:2 → C18:1 → C18:0



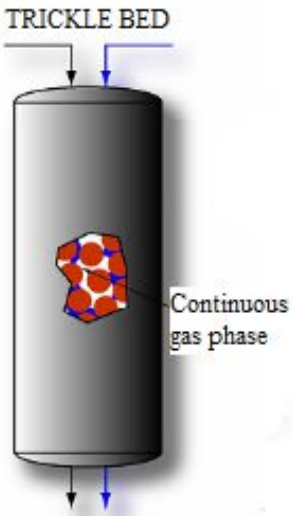
selectivity highly sensible to catalyst type, T & p_{H2}, but also hydrodynamics & mass transfer limitations

- **need for efficient & sustainable catalysts**

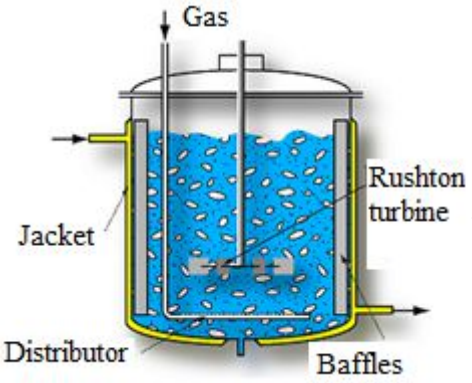
Motivation

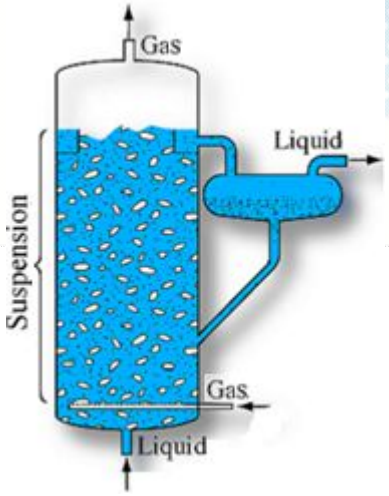
Drawbacks of conventional three-phase reactors:

Fixed bed reactor



Slurry reactor





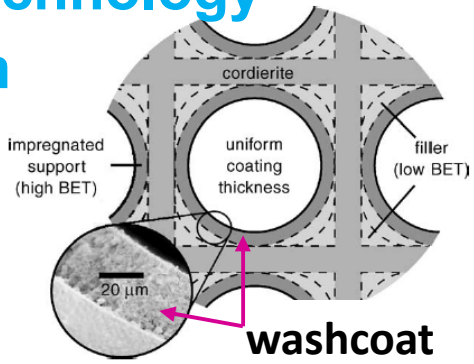
- *Liquid maldistribution (TBR)*
- *Partial catalyst wetting (TBR)*
- *Prone to hot spots and runaway (TBR)*
- *High resistances to mass transfer*
- *Limits of use for viscous/foaming fluids*
- *Plugging, high ΔP for small beads*

- *Uneasy catalyst separation, attrition*
- *Low ε_S & high mixing*
  - * *Reduced productivity*
  - * *Reduced selectivity (promotion of homogeneous side reactions & lower intermediate yields)*
- *High energy costs (mechanical stirring)*

Development of an innovative reactor for three-phase catalytic hydrogenation: HYDROMoRe project (ANR CD2I 2012)

Proposed solution

Innovative reactor inspired from monolith technology & equipped with *in situ* heat removal system



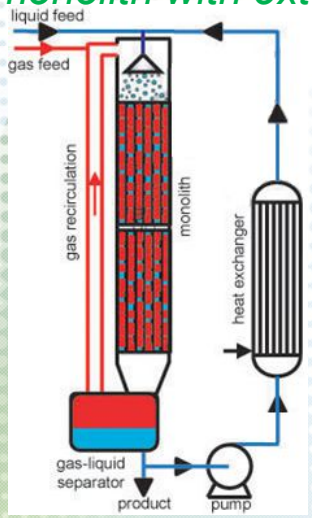
Kreutzer et coll., 2006

Expected features:

- Low ΔP
- Low diffusional limitations (**thin catalytic layer**)
- Good G-L & L-S mass transfer (**Taylor Flow**)
- Plug flow in channels (**TF**, ↑ productivity & selectivity)
- Fast draining in case of runaway

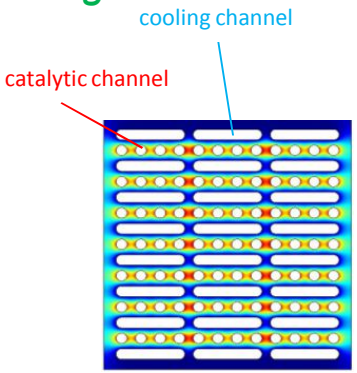
\+ Efficient temperature control (**quasi-isothermal**)

Ceramic monolith with external cooling



Kreutzer et coll., 2006
& US Patents, 1990s

Heat-exchanger Monolith Reactor



Catalytic channel walls:
heat conductive scaffold

Technological issues

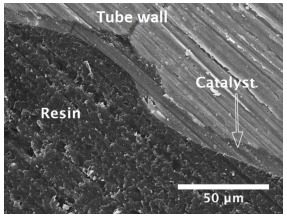
Monolith type reactor equipped with *in situ* heat removal system

- Conception of such a reactor with millimeter size channels and metal scaffold?

➢ **Manufacture by selective laser melting (Al alloy)**

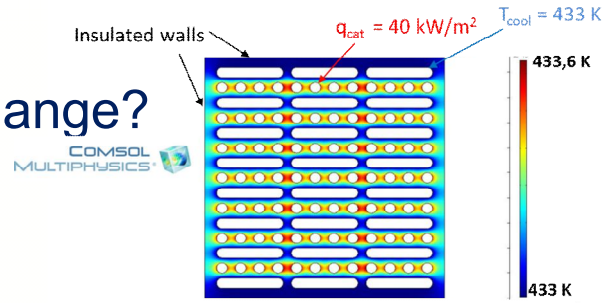
- Catalytic layer adherence, activity & stability?

➢ **Development of synthesis method & exhaustive characterizations**



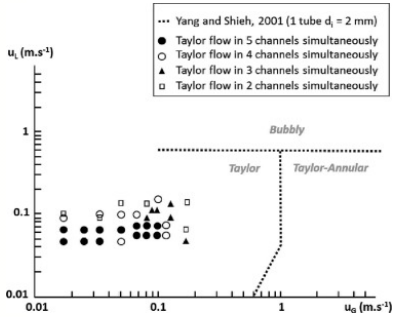
- Reactor design for efficient heat exchange?

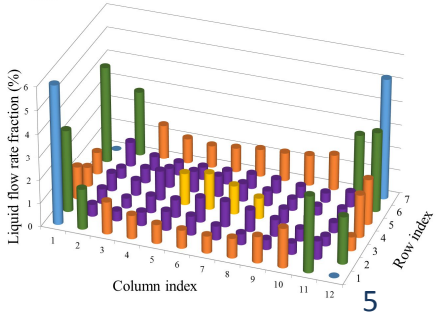
➢ **Simulation of thermal behavior**



- Suitable flow regime?

➢ **Design of suitable GL distributor & Experimental characterization of individual channel hydrodynamics** (cold mock-up)





Methodology
Catalytic objects & reactor tools

Continuous reactor

- **Efficient heat removal**

➢ **Single channel as relevant scale for the proof of concept**

with coated jacketed tubes

- **Is it enough?**

➢ Overall monolith performance strongly linked to the catalyst activity/selectivity **&** the hydrodynamic / mass transfer behavior of **individual channels**

➢ Need for a model that could **discriminate involved phenomena**

➢ **Intrinsic catalyst performance to be evaluated separately**

Stirred batch reactor

with coated platelets

☺ more representative of monolith washcoat
😐 need to be recycled for kinetic study (deactivation?)
☹ more difficult to characterize (M content)

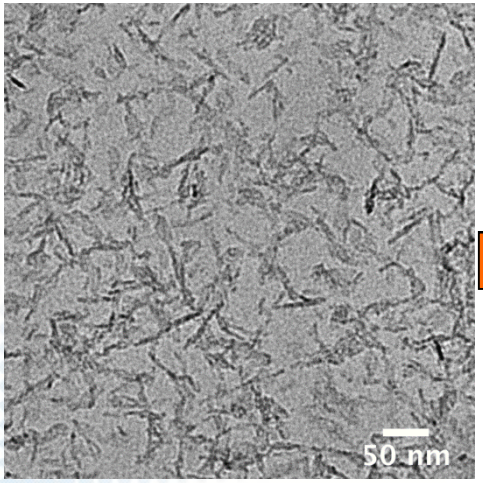
with catalytic powder

☺ homogenous lot, can be extensively characterized
☺ size and amount easily modified for kinetic regime
😐 same activity as washcoat?

Global overview of the coating process

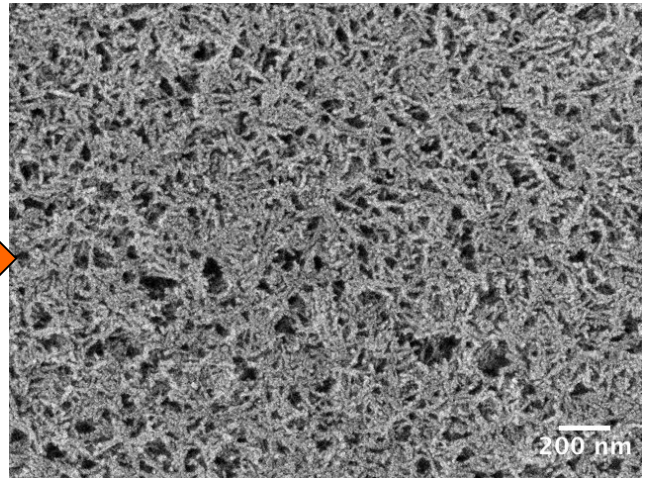
- Synthesis of colloidal dispersions (sols) of oxide nanoparticles in water
- Surface area and porosity are tuned through the addition of templating agents
- Sol deposition on the reactor walls (controlled filling and draining of the channel)
- Thermal treatment
- Impregnation with active metal precursor

AlOOH sol



AlOOH nanoparticles

500°C



Mesoporous alumina

Specific surface area : 300-500 $m^2 g^{-1}$

Average pore size : 5-40 nm

Pore volume : 0.3 - 2.6 $cm^3 g^{-1}$

Impregnation with active metal precursor

1 - Selective impregnation of Pd precursor on support (alumina)

- Pd acetylacetonate (Pd-acac) in toluene →

- $(NH_4)_2PdCl_4$ in water →

2 - Drying overnight at 70°C

3 - Activation by thermal treatment in H_2 for 30 min at 250°C

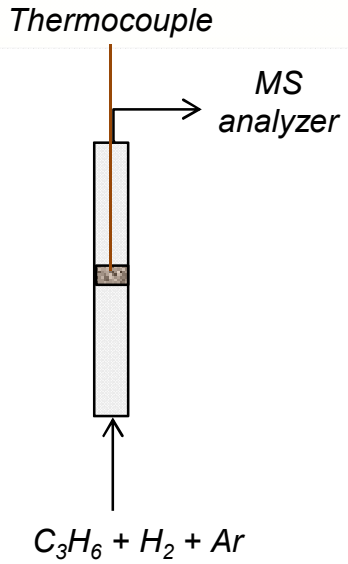
J.P. Boitiaux and J. Cosyns and S. Vasudevan, Studies in Surface Science and Catalysis, 16 (1983) 123.

Characterization of catalyst xerogel : propene hydrogenation

$$C_3H_6 + H_2 \leftrightarrow C_3H_8 \qquad \Delta H = -124\ kJ/mol$$

Conditions :

- Gas phase, P ≈ 1 atm
- Composition: 1% C_3H_6 + 1.5% H_2 in Ar
- Flow rate: 100 mL/min, temperature: ≈ 20°C
- Mass of catalyst = 10 mg mixed with 90 mg of alumina
- Analysis of outlet gas by mass spectrometry



Parameters :

- Active metal (Pd, Pt, Ru)
- Catalyst support (alumina vs. TiO_2)
- Addition of Pd (direct addition in sol vs. impregnation)
- Pd precursor : $(NH_4)_2PdCl_4$, Pd-acac in acetone, Pd-acac in toluene
- Thermal treatment temperature for decomposition (none to 300°C)
- Thermal treatment atmosphere for decomposition (Ar, O_2, H_2)

Results :

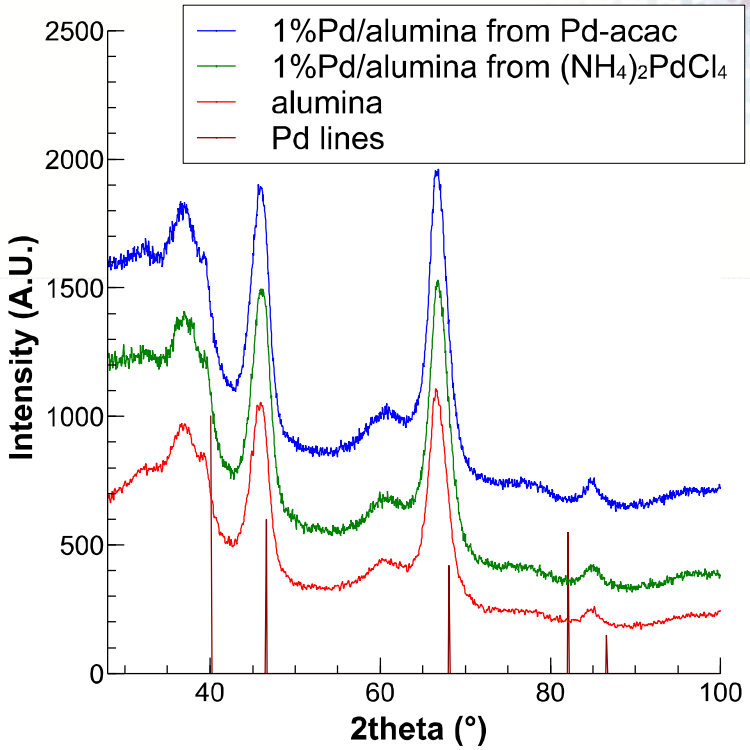
- Activity of catalysts prepared by impregnation >> direct addition in sol
- Toluene is a better solvent for Pd-acac than acetone
- Pd-acac gives more active alumina supported catalysts than $(NH_4)_2PdCl_4$
- With Pd-acac precursor TiO_2 and alumina are equivalent
- Best thermal decomposition conditions = H_2 at 250°C

Characterization of catalyst xerogel : SSA, XRD

S_{BET} and V_{pore} are determined from adsorption isotherms of N_2 at 77.4 K

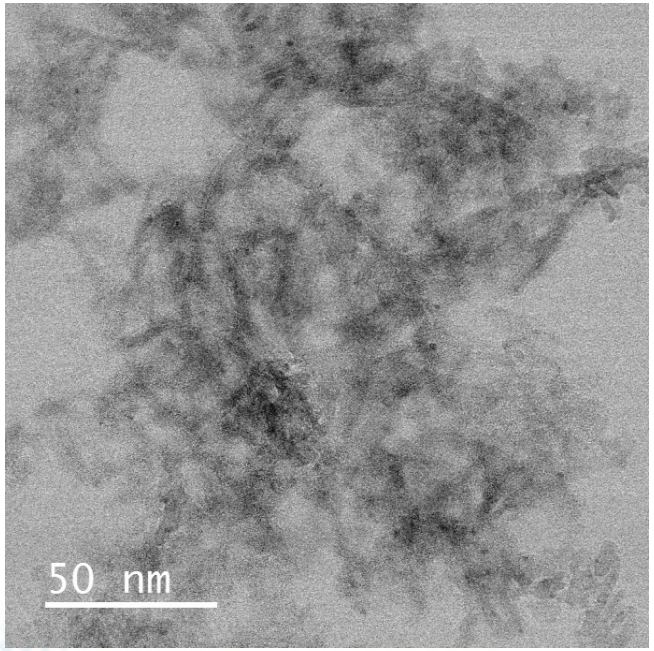
Xerogel	S_{BET} (m^2/g)	V_{pore} (mL/g)
Alumina	320 ± 20	1.2 ± 0.1
1%Pd/alumina from Pd-acac	320 ± 20	1.2 ± 0.1
1%Pd/alumina from $(NH_4)_2PdCl_4$	310 ± 20	1.2 ± 0.1

Negligible effect of impregnation on texture

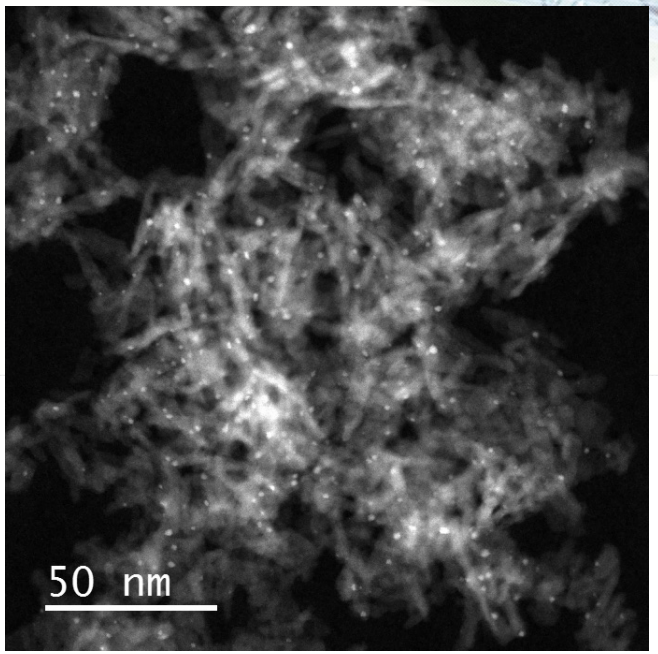


Crystallite size of Pd < 5 nm

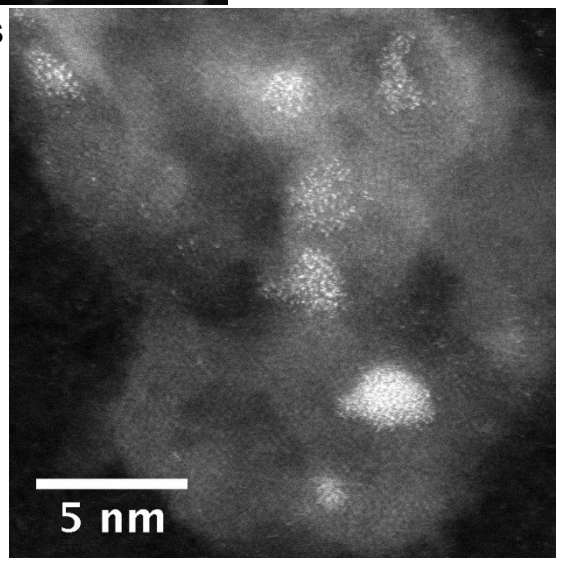
Characterization of catalyst xerogel : TEM



TEM : bright field image



STEM : dark field images



Catalyst : 1%Pd/alumina (from Pd-acac)

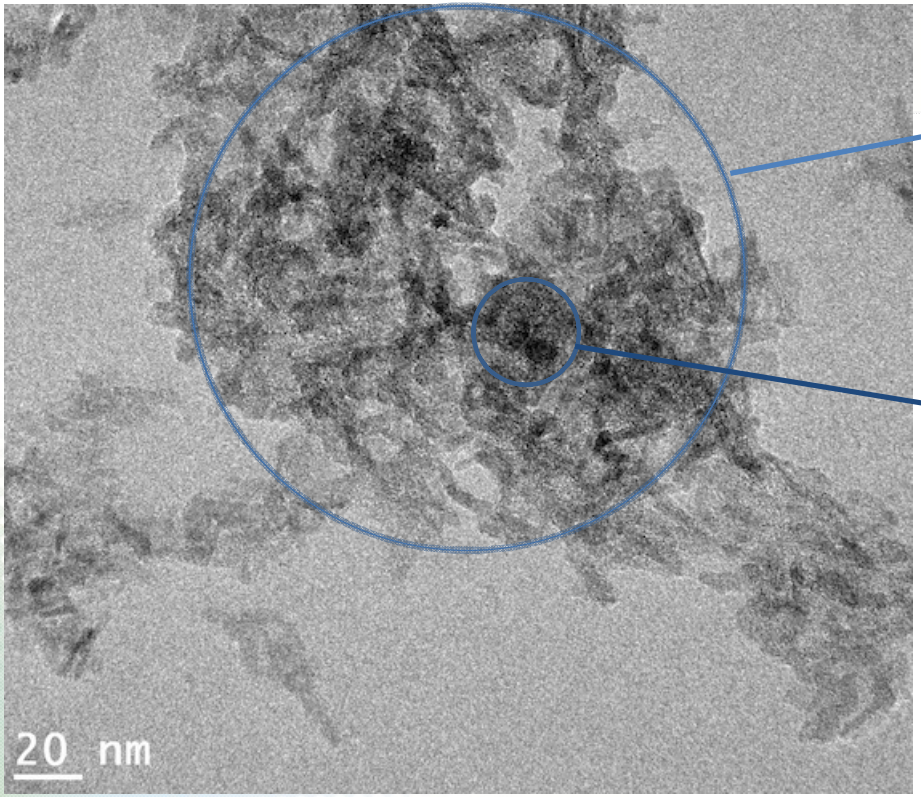
activated in H_2 for 30 min at 250°C

Microscope JEM-ARM200F Cold FEG

Characterization of catalyst xerogel : TEM

Catalyst : 1%Pd/alumina (from **$(NH_4)_2PdCl_4$**) activated in H_2 for 30 min at 250°C

Microscope JEM-2100F



EDX analysis gives 1%Pd

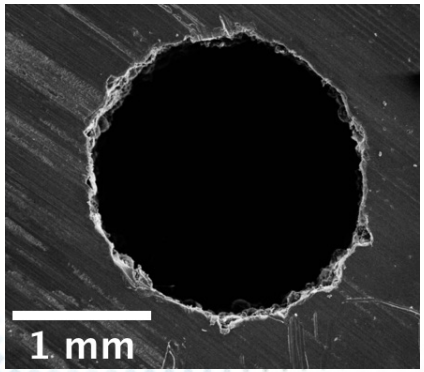
EDX analysis gives 1.7%Pd

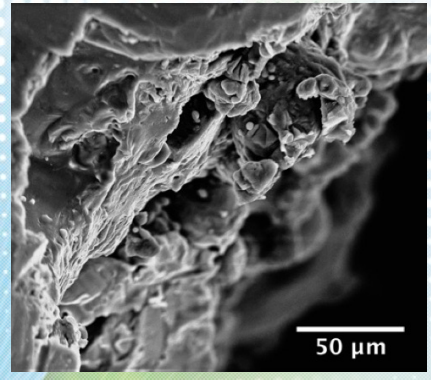
Characterization of coatings: SEM

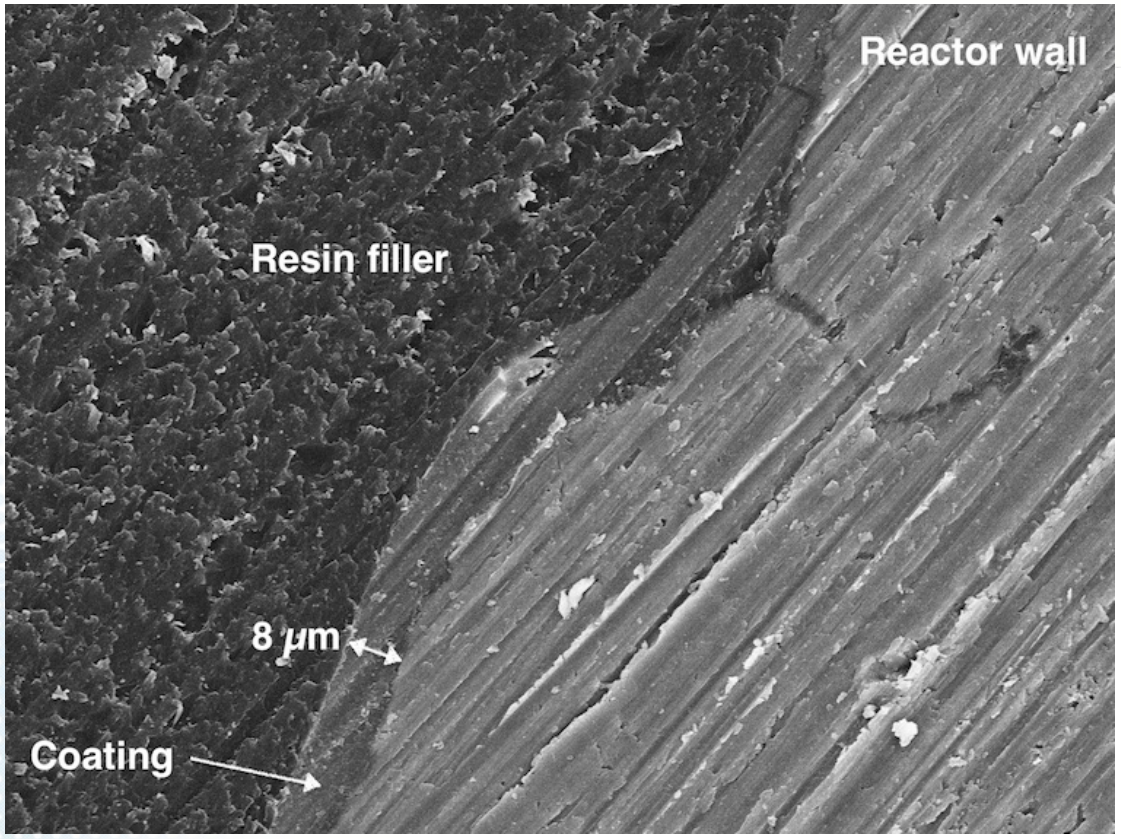
Determination of uniformity and thickness of the coating

1 - Filling the tube with epoxy resin

2 - Inspection by SEM of cross sections







Characterization of coatings: m/S, SSA

The coatings are well anchored, no loss was observed after adhesion tests

Coated amount of alumina (m/S) was evaluated by weighting

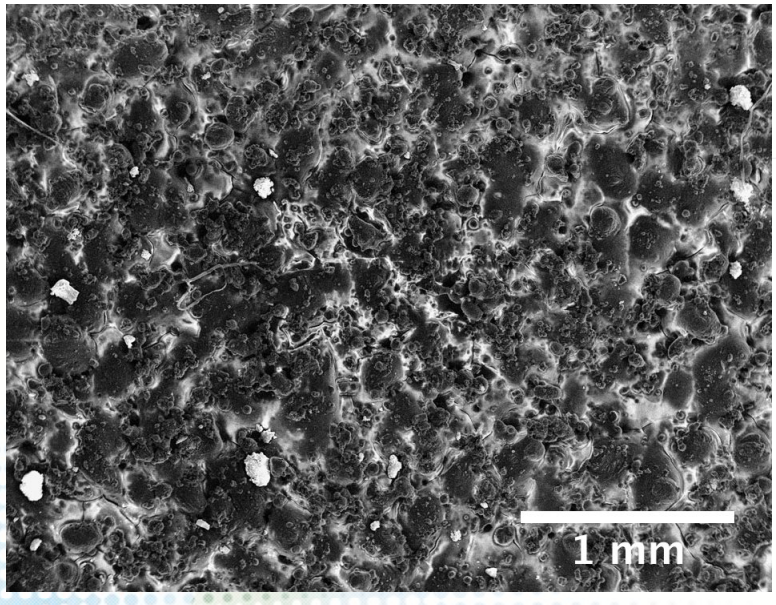
Substrate	Coated mass (mg)	m/S (g/m^2)
Al3003 platelets	3.6 ± 0.3	2.6 ± 0.2
AlSi10Mg platelets (SLM)	9.1 ± 0.3	3.8 ± 0.1
AlSi10Mg monotubes (SLM)	17 ± 5	14 ± 4

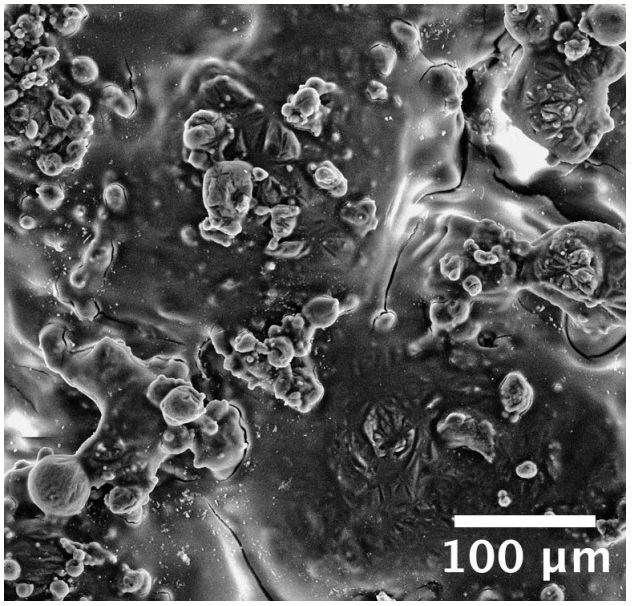
Surface area was determined from adsorption isotherms of Kr at 77.4 K

Substrat	Coated mass (mg)	Measured Surface (m^2)	Specific Surface Area (m^2/g)
AL3003 platelet	4	1.2	300
¼ AlSi10Mg monotube (SLM)	4	1.1	280

Characterization of coatings: SEM, EDS

EDS analyses done on SLM platelets after catalytic hydrogenation of α-pinene
- Check if the coating was damaged by the catalytic test
- Element analysis of Pd and S

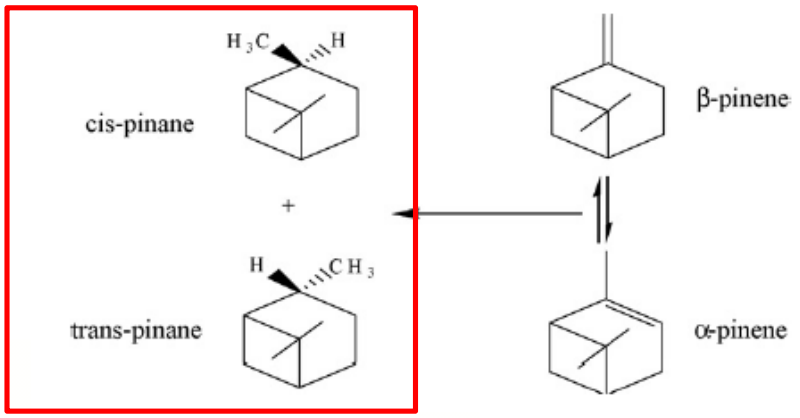




EDS analysis	S (wt.%)	Pd (wt.%)
Plate #1	0.33 ± 0.01	1.2 ± 0.3
Plate #2	0.0	1.6 ± 0.1
Plate #3	0.0	1.6 ± 0.3

Application to 3φ system

α-pinene hydrogenation:



Typical operating conditions:
p_{H2} = 1-100 bar, T = 50-200°C,
pure or diluted pinene (P),
Ni or noble metal catalyst

cis/trans selectivity reduced by an increase in temperature, but favored by increasing hydrogen pressure up to 10 bar (negligible effect beyond)

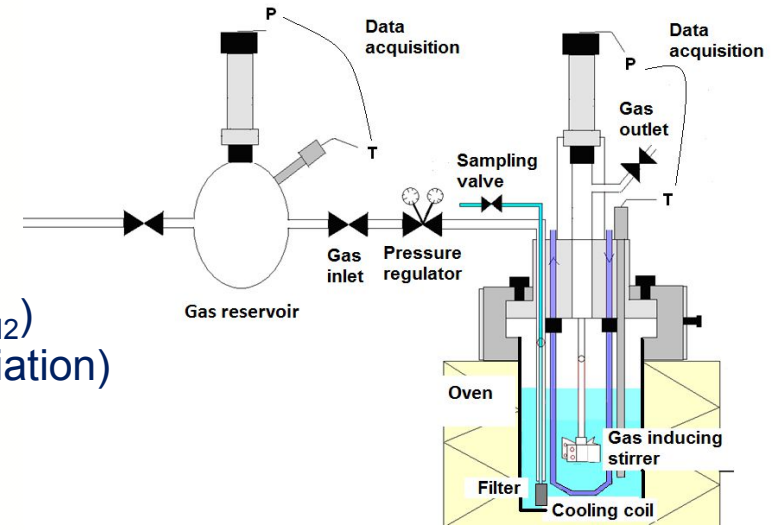
[Il'ina et coll., 2002; Simakova et coll., 2009; Wang et coll., 2015]

Kinetic investigation:

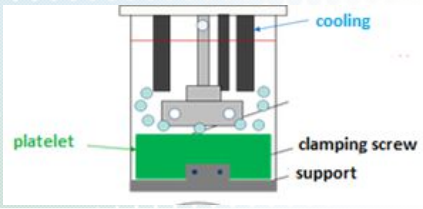
Stirred autoclave reactors (100 & 250 mL)
with **gas ballast** & **addition funnel**

- Controlled atmosphere (p_{H2}) and T
- Gas auto-dispersing stirrer (1200 rpm)
- Continuous recording of H_2 consumption ($R_{0,H2}$)

+ GC/FID analysis of L samples (product speciation)

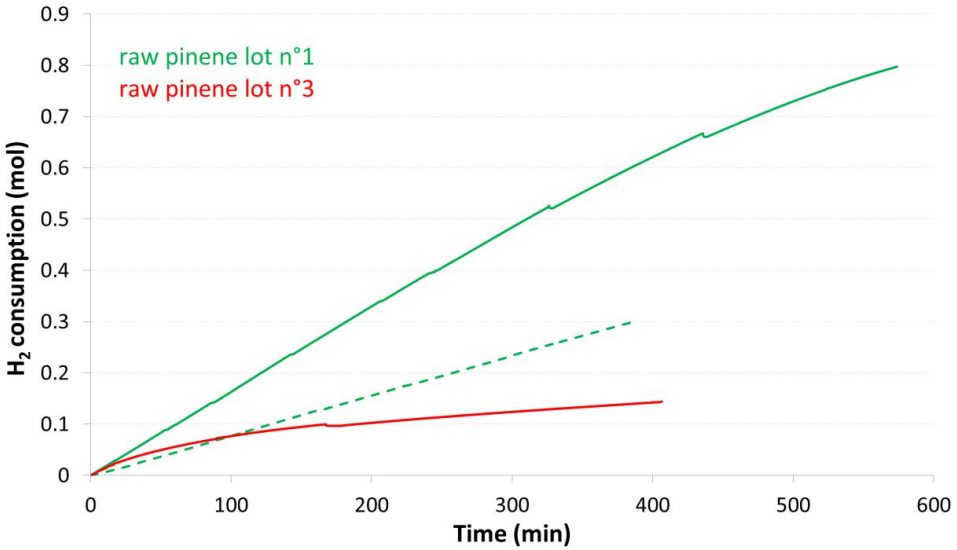


Catalytic platelet
(5-20 mg of coating)
or **powder** (5-50 mg)



Application to 3φ system
Deactivation issue

Preliminary tests (catalytic platelets):

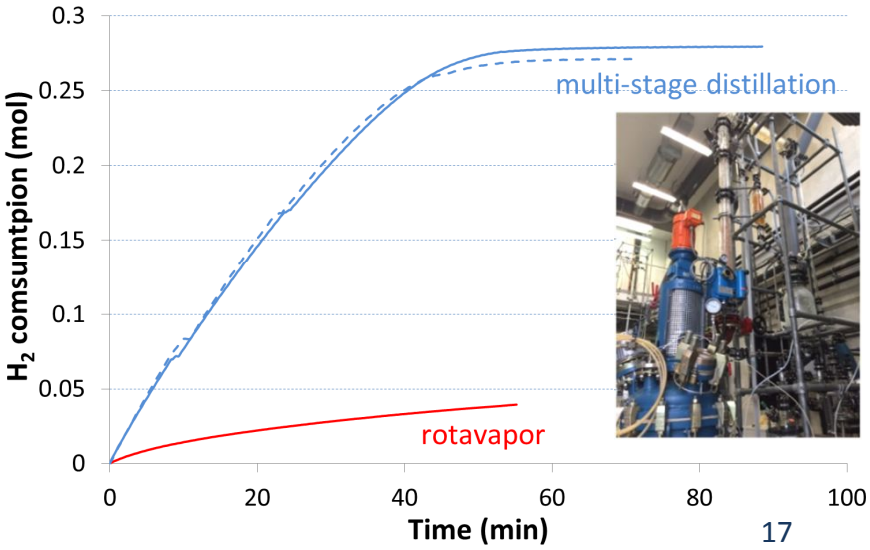


- Deactivation during the reaction or under recycling (---)
- Sulfur compounds and water traces initially suspected,

but S content < 0.4 ppm ∀ pretreatment of pinene, and molecular sieve not effective

Tests after distillation of raw pinene (powder):

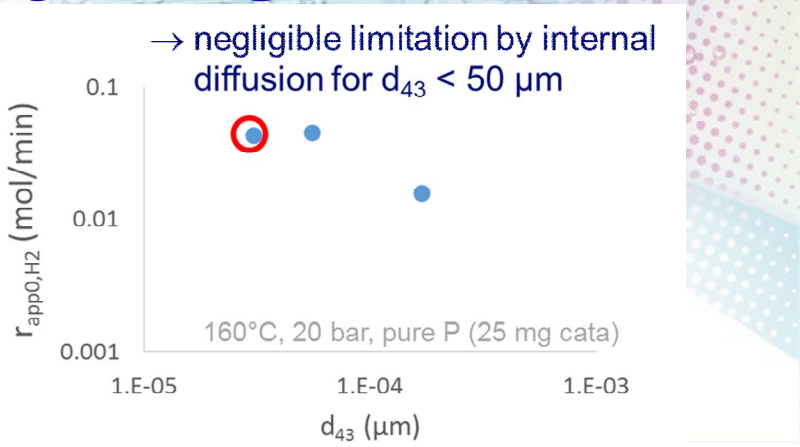
- Significant improvement of catalyst stability after batch **multi-stage distillation of pinene** (100 mbar)
- **Reproducible tests** (---)
- Deactivation by pinene oxidation products?



Pinene hydrogenation

Kinetic study (with powder):

➢ Experimental verification of **kinetic regime** (G-L mass transfer & internal diffusion)



➢ **Experimental database**: T = 100-160°C, p_{H2} = 10-30 bar, C_P = 1.5-6 mol/L, 50 mL liquid, 25 mg cata (d_{43} = 30 µm) → 18 experiments

➢ **Parameter study**: "apparent" E_A & react° orders in accordance with literature values

➢ **Reaction selectivity**: < 5% of β-pinene, cis-pinane selectivity: 60-70%
Evolution with T & p_{H2} in accordance with literature trends

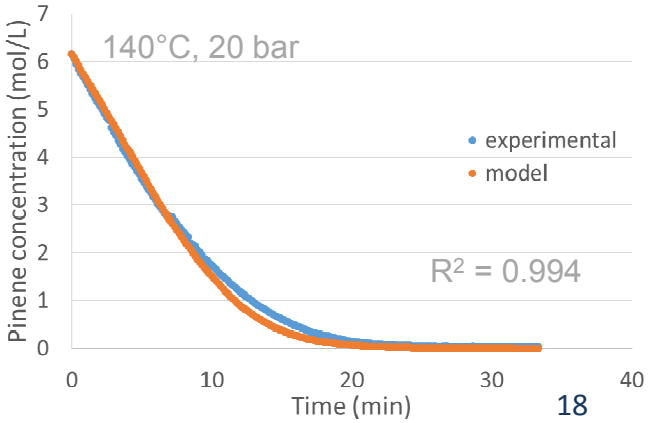
Modelling of intrinsic hydrogenation rate:

➢ Model discrimination & parameter estimation based on $\mathbf{R_{0,H2}}$ then **complete kinetic curves**

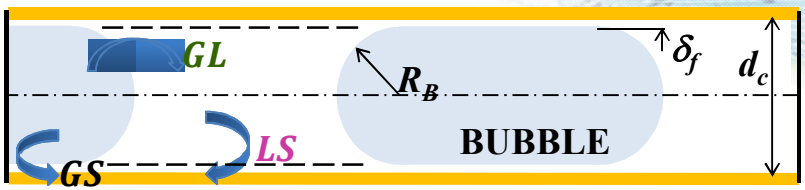
➢ **Selected model:**

$$R_{H2} = \frac{k K_{H_2} K_P P_{H_2} C_P}{(1 + \sqrt{K_{H_2} P_{H_2}} + K_P C_P)^3}$$

(dissociative adsorption of H_2, surface reaction as rate-determining step)

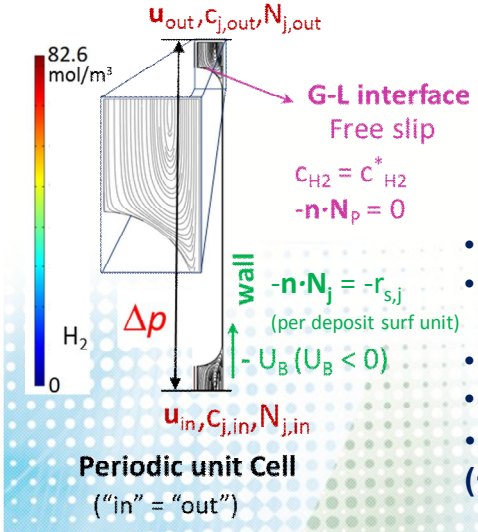


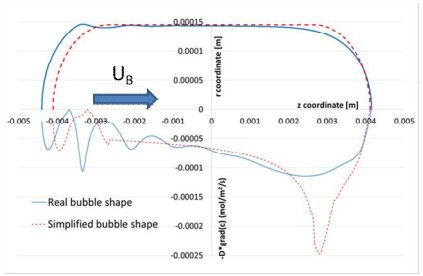
Capillary reactor modelling



Complex interplay in between mass transfer, local hydrodynamics & catalytic reaction

CFD model:





- Transient calculation
- No limitation by internal diffusion (e_{wc} ~10 µm)
- Isothermal cell
- Constant bubble shape & ε_G
- **1-phase or 2-phase calculations (→ relevant bubble shape)**

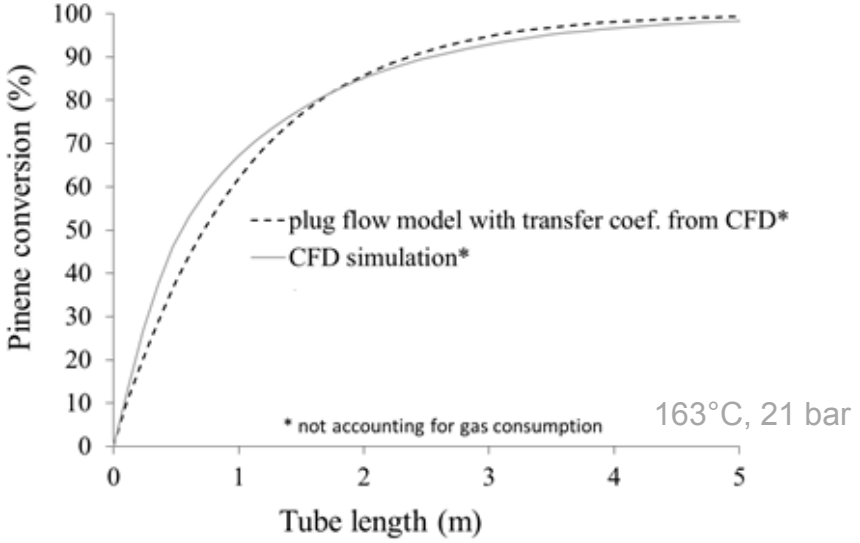
Individual mass transfer coefficients in agreement with literature, except k_{LS} for α–pinene (resistance underestimated by tested correlations)

Similar behavior of CFD & 1D models with adequate mass transfer coefficients

1D heterogeneous model:

Plug flow model describing external mass transfer resistances

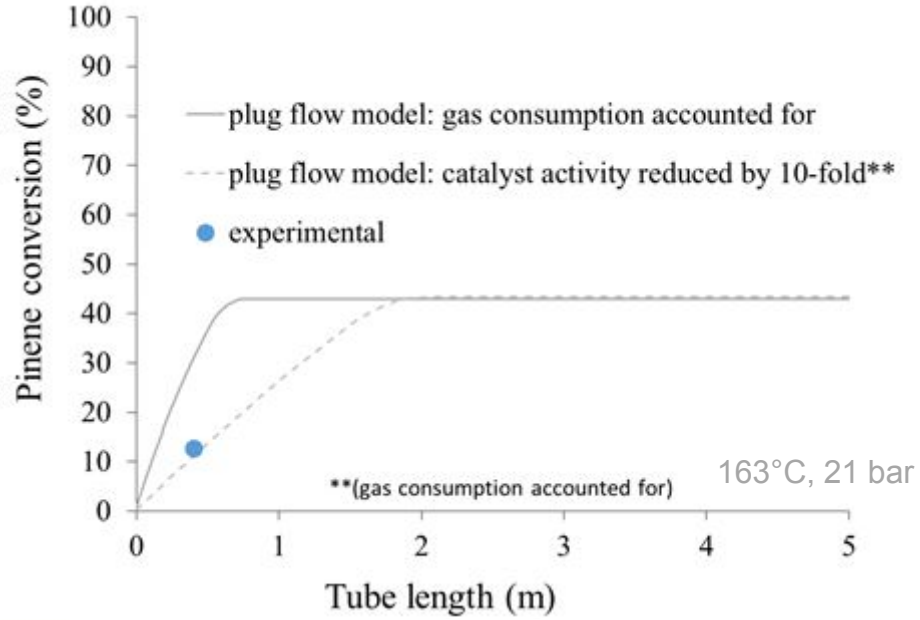
➢ can easily account for the effect of H_2 consumption



Comparison to reactor data & open questions

➢ Too optimistic predictions *vs.* measured conversion

Rem: cis-pinane selectivity= 35-70%

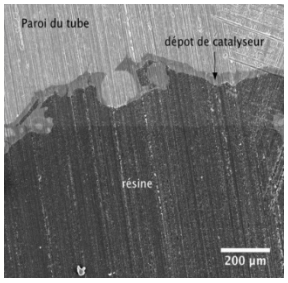


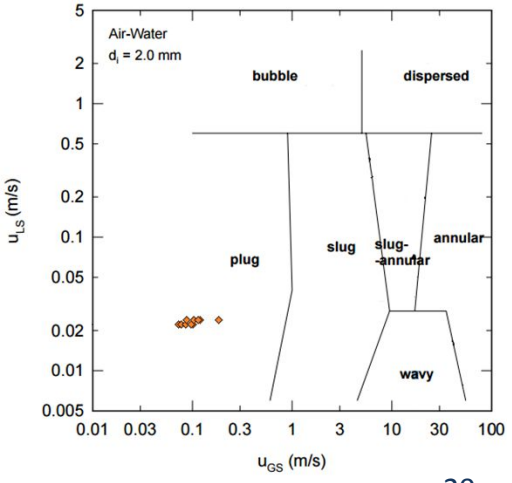
➢ Possible hypotheses:

- Taylor regime? (initial high ε_G? effect of wall roughness?)
- Overestimated k_La value? (geometry effect, arbitrary L_{UC})

- Impact of catalyst deactivation?
- Different activity of washcoat & powder?

Any suggestions?





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Thank you for your kind attention!